

CD221. LECTURE 17. NONIDEAL SYSTEMS

• The Imperfect Gas

The non-interacting systems we've been dealing with all this while are fine for illustrating general principles but they're not all that realistic. Real systems – and certainly the more interesting ones – tend to be interacting. We'll end our survey of statistical mechanics by discussing one example of how the formalism is applied to systems of this kind. The example we'll consider is the imperfect gas, which for the present purposes we'll understand to refer to a collection of N indistinguishable particles of mass m at constant temperature T in a box of volume V whose potential of interaction (the potential energy, in other words) is non-zero. Our objective will be to find its mechanical equation of state, i.e., the relation $P = P(T, V, N)$.

There are a great many *empirical* equations of state that have been found to satisfactorily describe gas behavior under conditions of high density, or low temperature, where the ideal gas law fails to hold. These equations typically take the form of *virial* expansions in the density, and can be expressed as

$$\frac{P}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots \quad (1)$$

where $\rho = N/V$, and the temperature-dependent factors $B_2(T)$, $B_3(T)$, etc., are so-called virial coefficients, $B_2(T)$ being the second virial coefficient and $B_3(T)$ the third virial coefficient. Virial coefficients are measures of how strong inter-particle interactions are, and how much the gas departs from ideality. A few actual values of these coefficients for argon at 25 C are shown in the Table below at increasingly high pressures.

P (atm)	$P/\rho k_B T$						
	1	+	$B_2\rho$	+	$B_3\rho^3$	+	remainder
	<hr/>						
1	1	−	0.00064	+	0.00000	+⋯	(+0.00000)
10	1	−	0.00648	+	0.00020	+⋯	(−0.00007)
100	1	−	0.06754	+	0.02127	+⋯	(−0.00036)
1000	1	−	0.38404	+	0.68788	+⋯	(−0.37232)

A question of immediate interest is whether Eq. (1) has any rigorous statistical mechanical basis. We'll consider this question now.

Since Eq. (1) is an equation for the pressure, and since we've assumed constant T , V and N conditions, a natural starting point for any statistical mechanical discussion of real gases is the classical canonical partition function Q , which as we've seen before is given by the following phase space integral

$$Q = \frac{1}{N!h^{3N}} \int d^3 q_1 \cdots \int d^3 q_N \int d^3 p_1 \cdots \int d^3 p_N e^{-\beta H(\{\mathbf{q}_i\}, \{\mathbf{p}_i\})} \quad (2)$$

where

$$H = \frac{1}{2m} \sum_{i=1}^N \sum_{\alpha=x,y,z} p_{i\alpha}^2 + V(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N). \quad (3)$$

Unlike the case of the ideal gas, the potential V (not the volume) is now no longer 0. But like the ideal gas, the momentum integrals of each individual particle in Eq. (2) can be carried out separately, the integral of the k th particle (for instance) being given by

$$\begin{aligned} \int d^3 p_k e^{-\beta \mathbf{p}_k^2 / 2m} &= \int_{-\infty}^{\infty} dp_{kx} \int_{-\infty}^{\infty} dp_{ky} \int_{-\infty}^{\infty} dp_{kz} e^{-\beta(p_{kx}^2 + p_{ky}^2 + p_{kz}^2) / 2m} \\ &= (2\pi m k_B T)^{3/2} \end{aligned} \quad (4)$$

There are N such factors arising out of the momentum integrations, and putting them all together, we see that Q becomes

$$Q = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{3N/2} \int d^3 q_1 \cdots \int d^3 q_N e^{-\beta V(\{\mathbf{q}_i\})} \quad (5)$$

If we multiply and divide this expression by V^N , we can write it as

$$Q = Q_{ideal} Z \quad (6)$$

where Q_{ideal} is the canonical partition function of the ideal gas, and Z is the so-called configuration integral, (or configuration partition function) defined as

$$Z = \frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N e^{-\beta V(\{\mathbf{q}_i\})} \quad (7)$$

The remainder of this discussion will be concerned with the evaluation (approximately) of this configuration integral.

• The Configuration Integral and its Approximate Evaluation

In the absence of an explicit form for the inter-molecular potential V , we must resort to approximations. As the first such approximation, we'll assume that the potential V can be separated into a sum of interactions between *pairs* of particles, in the following form

$$V = u_{12} + u_{13} + \cdots + u_{1N} + u_{23} + u_{24} + \cdots + u_{N-1,N} \quad (8)$$

where u_{ij} stands for the potential energy between particle i and particle j , which we'll assume depends only on the distance between them, $|\mathbf{q}_i - \mathbf{q}_j|$ (so their mutual orientation doesn't matter.)

If the above expression for V is substituted into Eq. (7), the configuration partition function becomes

$$Z = \frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N \prod_{pairs} e^{-\beta u_{ij}} \quad (9)$$

where \prod_{pairs} denotes a product over distinct pairs of particles. This is still a complicated expression, but things get better if we restrict our attention to the kinds of potentials u_{ij} that characterize molecules like neon or argon, or even hydrogen or nitrogen. These molecules tend to interact only when the distance separating them is small; at longer distances, they effectively don't know of each other's existence. For such molecules, u_{ij} looks roughly like this:

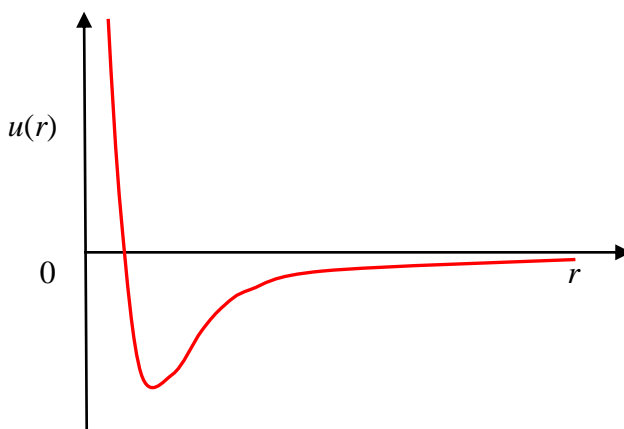


FIGURE 1

It's only in a narrow window of inter-particle separations that the molecules interact. For most other distances, then, $e^{-\beta u_{ij}}$ is very nearly 1, since $u_{ij} \approx 0$. Anticipating that we might want to make an approximation based on the smallness of the deviation of $e^{-\beta u_{ij}}$ from 1, let's introduce a function that measures this deviation. We define this function as

$$f_{ij} \equiv e^{-\beta u_{ij}} - 1 \quad (10)$$

The substitution of this definition into Eq. (9) leads to

$$Z = \frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N \prod_{pairs} (1 + f_{ij}) \quad (11)$$

where the product over pairs of particles takes the following explicit form

$$\prod_{pairs} (1 + f_{ij}) = (1 + f_{12})(1 + f_{13}) \cdots (1 + f_{1N})(1 + f_{23})(1 + f_{24}) \cdots (1 + f_{N-1,N}) \quad (12)$$

If we multiplied these factors out, the first term we'd get would be 1; then there would a number of terms involving just a single f function; then a number of terms involving a product of two f functions; and so on. In other words,

$$\prod_{pairs} (1 + f_{ij}) = 1 + \sum_{pairs} f_{ij} + \sum_{\substack{distinct \\ pairs}} f_{ij} f_{kl} + \cdots \quad (13)$$

And so, after putting Eq. (13) back into Eq. (11), we obtain

$$Z = \frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N \left(1 + \sum_{pairs} f_{ij} + \sum_{\substack{distinct \\ pairs}} f_{ij} f_{kl} + \cdots \right) \quad (14)$$

From the way we've defined f , we know that it will be small for most intermolecular separations, which means that keeping just the first couple of terms in the expansion above should give us a reasonably good description of Z . In fact, we'll now drop the contributions from the terms involving two and higher factors of f , and see how far that gets us. So with this simplification Eq. (14) becomes

$$Z \approx \frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N \left(1 + \sum_{pairs} f_{ij} \right) \quad (15)$$

Let's now we turn to the explicit evaluation of the individual terms in Eq. (15). The first term (corresponding to the factor of unity) is easy to evaluate – each of the integrals $\int d^3 q_i$, $i = 1, 2, \dots, N$, yields a factor of the volume V . Hence,

$$\frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N = 1 \quad (16)$$

In each of the next terms in Eq. (14), which contain one factor of the f function, only two of the integration variables will be the same as the variables that appear in the function.

An example of such a term is the following: $\frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N f_{12}$. Here, all the integrations except those for \mathbf{q}_1 and \mathbf{q}_2 can be carried out at once, giving

$$\begin{aligned} \frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N f_{12} &= \frac{1}{V^N} V^{N-2} \int d^3 q_1 \int d^3 q_2 f_{12} \\ &= \frac{1}{V^2} \int d^3 q_1 \int d^3 q_2 f_{12} \end{aligned} \quad (17)$$

At the same time, since it doesn't matter which particles are labelled 1 and 2, every one of the other terms containing just a single f function is equal to the one we've considered as an example. So if we added all these terms together, we'd get the result in Eq. (17) multiplied by the number of distinct pairs.

How many distinct pairs are there? This is the same as asking for the number of combinations of the numbers (ij) , with $i, j = 1, 2, \dots, N$ and $j \neq i$. There are N ways to pick i , and having picked a number, there are then $N-1$ ways to pick j , for a total of $N(N-1)$ ways to pick the pair (ij) . But this includes contributions that differ only by a simple interchange of numbers (like the pairs 37 and 73, which are not distinct.) So the number of distinct pairs is just $N(N-1)/2$. The second term in Eq. (15) is therefore given by

$$\frac{1}{V^N} \int d^3 q_1 \cdots \int d^3 q_N \left(\sum_{pairs} f_{ij} \right) = \frac{N(N-1)}{2V^2} \int d^3 q_1 \int d^3 q_2 f_{12} \quad (18)$$

Our "first order" approximation for Z is therefore

$$\begin{aligned} Z &= 1 + \frac{N(N-1)}{2V^2} \int d^3 q_1 \int d^3 q_2 f_{12} \\ &\equiv 1 + I \end{aligned} \quad (19a)$$

where

$$I = \frac{N(N-1)}{2V^2} \int d^3 q_1 \int d^3 q_2 \left(e^{-\beta u_{12}} - 1 \right). \quad (19b)$$

As a further approximation, since we've assumed that I is small, we can write Eq. (19a) in exponential form (because some time later we'll take logs, and having an exponential to take the log of makes life a little easier). Thus

$$Z \approx \exp \left[\frac{N(N-1)}{2V^2} \int d^3 q_1 \int d^3 q_2 (e^{-\beta u_{12}} - 1) \right] = e^I \quad (20)$$

We're now in a position to put the various pieces of our calculation together and to make some thermodynamic connections.

• The Thermodynamic Connection

Before anything else, let's try and simplify the integral I , defined in Eq. (19b). Since u_{12} depends only on the distance between particles 1 and 2, i.e., $u_{12} = u_{12}(|\mathbf{q}_1 - \mathbf{q}_2|)$, we can introduce a new variable $\mathbf{q} = \mathbf{q}_1 - \mathbf{q}_2$ into the equation, and change variables in the second integral from \mathbf{q}_2 to \mathbf{q} . We can also approximate $N-1$ by N since $N \gg 1$. These changes produce

$$I = \frac{N^2}{2V^2} \int d^3 q_1 \left[\int d^3 q (e^{-\beta u(q)} - 1) \right] \quad (21)$$

where q is the magnitude of \mathbf{q} . Now the integral over \mathbf{q}_1 can be carried out, and it leads to a factor of the volume V . Thus,

$$I = \frac{N^2}{2V} \int d^3 q (e^{-\beta u(q)} - 1) \quad (22)$$

If we substitute this expression into Eq. (20), put the result into Eq. (6) and then take logs, we obtain the following expression for the Helmholtz potential F

$$\begin{aligned} F &= -k_B T [\ln Q_{ideal} + I] \\ &= -k_B T \left[-\ln N! + \frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + N \ln V + \frac{N^2}{2V} \int d^3 q (e^{-\beta u(q)} - 1) \right] \end{aligned} \quad (23)$$

Since we're after the mechanical equation of state, we must use Eq. (23) to get the pressure. Recalling that $dF = -SdT - PdV + \mu dN$, we see that we can obtain P as $P = -(\partial F / \partial V)_{T,N}$. So differentiating Eq. (23) with respect to V at constant T and N , we obtain

$$P = \frac{Nk_B T}{V} - \frac{N^2 k_B T}{2V^2} \int d^3 q (e^{-\beta u(q)} - 1) \quad (24)$$

which we can write as

$$\frac{P}{k_B T} = \rho - \frac{\rho^2}{2} \int d^3 q (e^{-\beta u(q)} - 1) \quad (25)$$

Comparing Eqs. (1) and (25), we see that we have indeed reproduced the form of the empirical equation of state provided we define the second virial $B_2(T)$ as

$$B_2(T) = -\frac{1}{2} \int d^3 q (e^{-\beta u(q)} - 1) \quad (26)$$

It now remains to see whether with this expression for the second virial coefficient we can make testable predictions of imperfect gas behavior. We'll take up this question next.

• Models of the Second Virial Coefficient

Since the integrand in Eq. (26) depends only the magnitude of the distance between the particles, q , we can simplify it by transforming to spherical polar coordinates, i.e., we make the change of variables $(q_x, q_y, q_z) \rightarrow (q, \theta, \phi)$, where $q_x = q \sin \theta \cos \phi$, $q_y = q \sin \theta \sin \phi$, and $q_z = q \cos \theta$. This gives us

$$\begin{aligned} B_2(T) &= -\frac{1}{2} \int_{-\infty}^{\infty} dq_x \int_{-\infty}^{\infty} dq_y \int_{-\infty}^{\infty} dq_z (e^{-\beta u(q)} - 1) = -\frac{1}{2} \int_0^{\infty} dq q^2 \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin \theta (e^{-\beta u(q)} - 1) \\ &= -2\pi \int_0^{\infty} dq q^2 (e^{-\beta u(q)} - 1) \end{aligned} \quad (27)$$

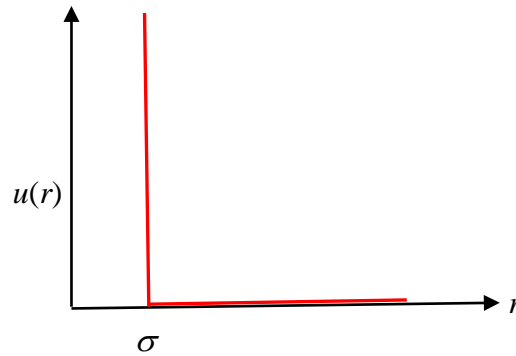
To proceed further, a definite functional form of the intermolecular potential must be specified. From what we have indicated earlier, this potential must essentially vanish at large distances, and become quite steeply repulsive at short distances, with an intermediate regime where it is attractive. Several models of $u(q)$ have been proposed. We'll look at a selection of them.

(i) The hard sphere potential

This is an idealized potential that is identically 0 everywhere except within a distance σ of the particle, where it is infinite. That is, (and now we'll switch to the more conventional symbol r for intermolecular distances):

$$u(r) = \begin{cases} 0, & r \geq \sigma \\ \infty, & r < \sigma \end{cases} \quad (28)$$

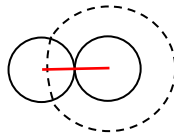
The potential looks like this:



For this potential, B_2 is found by substituting Eq. (28) into Eq. (27) and carrying out the integrals. The result is

$$\begin{aligned} B_2(T) &= -2\pi \int_0^\sigma dr r^2 (e^{-\infty} - 1) - 2\pi \int_\sigma^\infty dr r^2 (1 - 1) \\ &= \frac{2\pi\sigma^3}{3} \end{aligned} \quad (29)$$

The parameter σ in the hard sphere potential can be interpreted as the distance of closest approach of two particles, which is the length of the red line below:



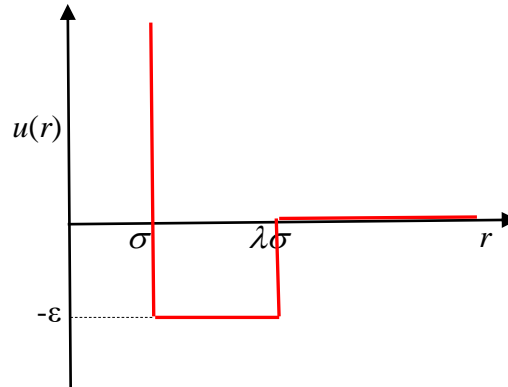
This distance is the radius of a sphere from which the particle on the left is *excluded*. The volume of this sphere is $4\pi\sigma^3/3$, so the second virial coefficient in the hard sphere model is just half the excluded volume. It has no temperature dependence.

(ii) The Square Well Potential

The hard sphere potential had no attractive component. A slight improvement on this model is the square well potential, defined as

$$u(r) = \begin{cases} \infty, & r < \sigma \\ -\varepsilon, & \sigma \leq r \leq \lambda\sigma \\ 0, & r \geq \lambda\sigma \end{cases} \quad (30)$$

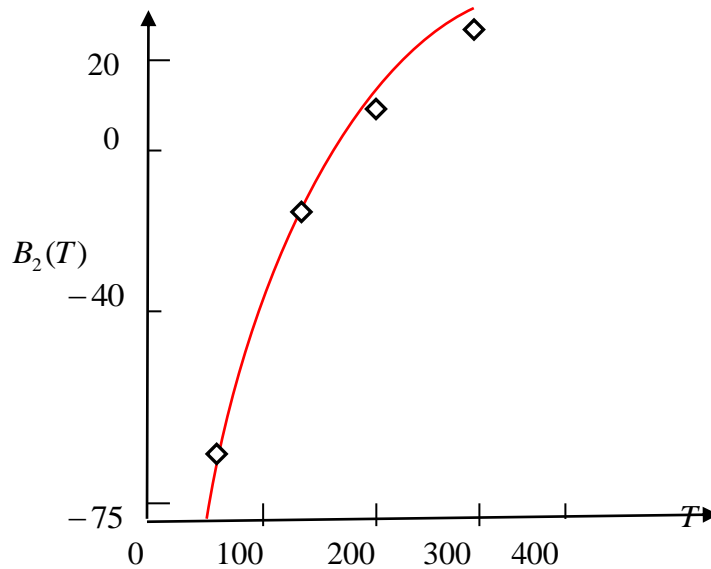
This potential looks like this



The second virial coefficient for this potential is similarly found by substituting Eq. (30) into Eq. (27) and carrying out the integrals:

$$\begin{aligned} B_2(T) &= -2\pi \int_0^{\sigma} dr r^2 (e^{-\infty} - 1) - 2\pi \int_{\sigma}^{\lambda\sigma} dr r^2 (e^{\beta\varepsilon} - 1) - 2\pi \int_{\lambda\sigma}^{\infty} dr r^2 (1 - 1) \\ &= \frac{2\pi\sigma^3}{3} - \frac{2\pi}{3} (e^{\beta\varepsilon} - 1)(\lambda^3\sigma^3 - \sigma^3) \\ &= \frac{2\pi\sigma^3}{3} [1 - (e^{\beta\varepsilon} - 1)(\lambda^3 - 1)] \end{aligned} \quad (31)$$

This expression – despite the simplemindedness of the model that underlies it – fits experimental data on virial coefficients remarkably well, as the following graph (adapted from Fig. 12-5 McQuarrie) attests:



The solid red line is the theoretical prediction of the square well model (after suitable adjustment of the parameters ε , σ and λ for best fit), and the open diamonds are data on argon.

(iii) A still more realistic potential is the so-called Lennard-Jones potential, given by

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (32)$$

It has exactly the shape given by Fig. 1, but an analytic expression for B_2 can no longer be obtained from it. But as we've seen, the square well model itself does a good job of reproducing the trends in experimental data, and no new insights emerge from the use of Eq. (32) in the calculation of B_2 .

The method of expanding a potential energy function in powers of some small quantity goes by the name of perturbation theory. It is central to the statistical mechanical treatment of interacting systems, and can be applied to systems as different as polymers, electromagnetic fields, or critical point fluids.